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DIRECTION OF REACTION OF PEROXIDE FORMATION ON
A STRAIGHT ALKANE CHAIN. PEROXIDE FORMED IN
AUTO-OXIDATION OF NORMAL HEPTANE

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[The material presented by the authors is of interest from the viewpoint of reaction kinetics of explosions and combustion. Furthermore, n-alkane peroxides potentially may be used as components of fuels or propellant mixtures.]

Although the direction of the attack of molecular oxygen on molecules of isoalkanes, cyclanes, alkanes, alkyl-substituted aromatics, and naphthene-aromatic hydrocarbons in the beginning stage of their auto-oxidation has been to a large extent clarified [1], the problem concerning the point at which the O_2 is included in the simplest hydrocarbon structure -- a straight alkane chain -- is as yet unsolved.

The majority of hypotheses assumes that the oxidation begins with the carbon atom at the end of the chain [2-5 and many others], but substantial proof of this contention has not been given. Results of the experimental work of Pope and his collaborators [2], dealing with the vapor-phase oxidation of alkanes, are not reliable since they used imperfect methods for the separation and analysis of the reaction products. In fact, as far as the composition of the products is concerned, their results had to be revised in the light of subsequent, more accurate investigations. For example, as a result of the oxidation of n-heptane in the vapor phase [6], a 30% yield of peroxides (based on the original hydrocarbon) was obtained, and it was also shown that a large quantity of ketones was formed, particularly in the opening stage of the process. However, the ketones and peroxides claimed by Pope et al. were not found at all.

Ketones cannot be formed as a result of the oxidation of the end C atoms of a hydrocarbon chain. Therefore, considering this fact, as well as recent information to the effect that auto-oxidation of hydrocarbons at moderate temperatures always begins with attachment of molecular oxygen at the aliphatic

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or alicyclic C-H bond, and finally, the fact that the stability of the primary C-H bond is greater than that of the secondary, it seems probable that peroxide formation at the straight alkane chain should begin, not at the end, but on one of the intermediate members of the chain, and that it is accompanied by the formation of secondary hydroperoxide.

To check this assumption, Ivanov and his co-workers set out to investigate the oxidation of n-heptane in the liquid phase at a low temperature, the main purpose being the isolation of the original formed peroxide, the structure of which should give an indication as to the direction of the initial stage of the oxidation process.

First experiments revealed an unusual stability of n-heptane under these conditions, while in the vapor phase the hydrocarbon had been easily oxidized even at a lower temperature than that required for the aromatic and cyclane hydrocarbons with the same number of carbons atoms [7]. The use of catalysts (organic salts of Mn, CrO₃, etc.) did not prove effective. Exposure to ultraviolet light, successfully used [1] to prepare peroxide of isoalkanes and cyclanes (which are oxidized with difficulty) did not significantly accelerate the process. The concentration of peroxides in the reaction mixture at first slowly increased, attained 0.5-0.6% in 150 hours, and remained almost constant during the course of the remaining period of oxidation (400 hours or more).

This characteristic of the kinetics of oxidation of heptane, depending, apparently, on the retarding effect of the products of partial decomposition of peroxide (resulting from the extended length of the experiment of oxidation), and also the difficulty in the extraction of peroxide from products of the reaction, due to its very small concentration and the presence of admixtures (distillation for purposes of separation of this admixture were not successful), greatly complicated its separation in the pure form in a quantity sufficient for investigation. Nevertheless, the authors used their own method to have the peroxide of heptane selectively absorbed by an aqueous solution of an alkali and succeeded in extracting it from the oxidized hydrocarbon. Thus, they accumulated a quantity of it, and after repeated distillations in vacuum, prepared a total of about 4.5 g of pure peroxide of n-heptane.

This compound is a transparent, rather mobile, colorless liquid with a pleasant odor, only partially reminiscent of the odors of heptane, having in conformity with the data for the elementary composition and molecular weight, the formula C₇H₁₄O₂. The content of active oxygen corresponding to one peroxide group, and the energetic reaction with lead tetraacetate characterizes it as a monatomic hydroperoxide.

To determine the position of -OO-H group, the hydroperoxide was decomposed by boiling it with alkali, as a result of which it was converted into heptanone-2 (70%) and heptanol-2 (about 30%). A somewhat lesser quantity of the same ketone was formed by the action of Pb(O·CO·CH₃)₄ or FeSO₄ on the hydroperoxide.

Therefore, it follows that the peroxide formed in the initial stage of oxidation of n-heptane with molecular oxygen is the hydroperoxide (I) with an -OO-H group attached in position 2 to atom in the resulting molecule of heptane-hydroperoxide-2, the decomposition of which (under the action of an alkali) proceeds mainly according to the scheme (II), characteristic for secondary hydroperoxides; and further that the direction of the main reaction can be expressed by the scheme (III).

The three formula schemes are as follows:

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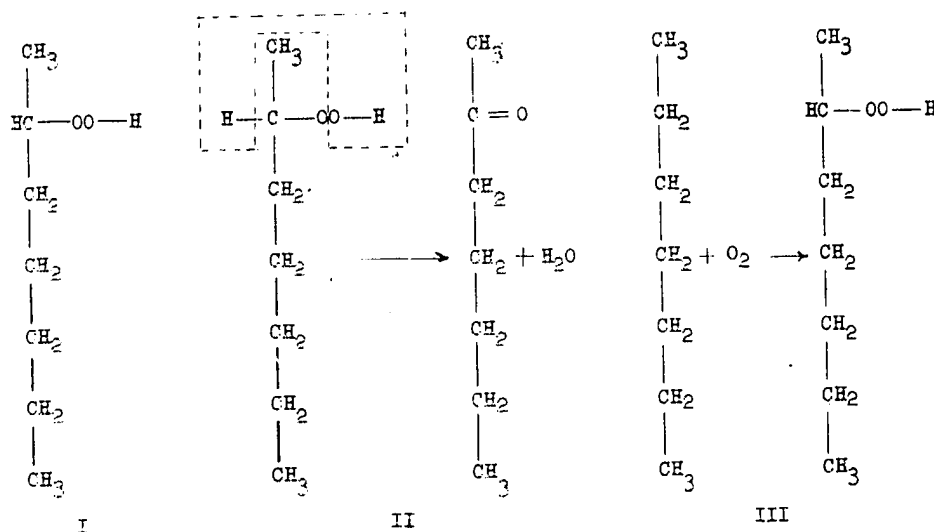
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Preparation of the Peroxide of n-Heptane

Standard n-heptane with the following properties was used as the starting material: bp 98.4° at 760 mm; solidification point, -90.65°; $d_4^{20} = 0.6838$; and $n_D^{20} = 1.3877$. A batch of 120-150 g of this hydrocarbon was oxidized at 80° in a quartz flask with a capacity of 300-350 ml, equipped with very effective condenser coils, by bubbling oxygen at the velocity of ml/min under exposure to ultraviolet light for 120-150 hours in an apparatus described earlier [1]. Then the main quantity of unreacted heptane was distilled off from the reaction product at 4-10 mm and room temperature. The combined concentrates (6-8 portions), (containing 6-7% peroxide), were treated three times with a 7% aqueous solution of NaOH. Next, the combined alkaline extracts were instantly saturated with sodium sulfate and extracted (4 times) with distilled ether. The organic acids present in small quantities in oxidized heptane were extracted simultaneously with the peroxide, and were separated as a result of this to remain in the form of salts in the alkaline solution. From the ether extracts, after drying them with calcined sulfate, the solvent was distilled at reduced pressure. The residue was maintained 2 hours in a current of nitrogen at one mm and at room temperature and then was distilled in a high vacuum from a Claisen flask made of molybdenum glass with a wide outlet tube attached to it (the temperature of the heating water bath not higher than 58° and the receptacles cooled to -50°). The main fraction, distilled at 38° at 0.08 mm is the peroxide of n-heptane (yield of 0.2-0.3% with respect to the original hydrocarbon); $d_4^{20} = 0.9072$; $n_D^{20} = 1.4305$; σ' (specific dispersion) = $\frac{n_F - n_C}{d} 10^4 = 86.6$.

The peroxide gives an intensive qualitative reaction for active oxygen with KI or a thiocyanate solution and for the hydroxyperoxide group with lead tetraacetate. n-Heptane hydroperoxide is stable and unaffected by storage. It is easily soluble in ether, alcohol, benzene, petroleum ether, and dilute aqueous alkali. It is insoluble in water.

Decomposition of n-Heptane Hydroperoxide

The substance was decomposed by boiling under reflux with 10% NaOH. Its decomposition products were isolated as semicarbazones and identified by taking melting points of mixtures of the latter with semicarbazones of known substances. The results are listed in the attached table.

The heptanone-2, formed by the interaction of n-heptane hydroperoxides with lead tetraacetate or ferric sulfate, was also identified by this method.

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Table 1

mp in °C

<u>Initial Carbonyl Compound</u>	<u>Semicarbazones According to Previously Published Data</u>	<u>Data of Ivanov and Co-workers</u>	<u>Mixture (1.1) of semicarbazone with semicarbazone of carbonyl compound No 1 (mp 119°C)</u>	<u>Depression of mp in °C</u>
Produced in decomposition of hydrogen peroxide of:				
n-heptane	--	119	--	--
enanthol	109	111	94.5	16.5
heptanone-2	123,127	124	120.2	none
heptanone-3	102	103	93	10
heptanone-4	133	136	97	22

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